

**INTERPRETATION OF SPECTRA OF DISPERSIONS - A HYBRID
APPROACH TO ACCOUNT FOR INTER-PARTICLE INTERACTIONS**

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ABSTRACT

The problem of extracting quantitative information on individual particle properties from spectroscopic measurements conducted at concentrations where particle interactions become significant is of great industrial and theoretical importance. For dispersions of charged particles, this could happen at fairly low concentrations. To interpret light scattering spectra of such dispersions, the effect of the fluid (slurry) structure has to be taken into account. In this paper, a hybrid method that addresses the effect of the fluid structure is proposed. The hybrid approach describes the fluid structure by relating the “effective” Percus-Yevick hard-sphere parameters to system parameters using empirical models. This approach is examined with data generated by Monte Carlo simulations of charged spherical particles using realistic interaction potentials.

Keywords: Particle characterization, Percus-Yevick Approximation, Light Scattering,

1. INTRODUCTION

Colloidal systems have been extensively studied by scattering methods using electromagnetic radiation (light and x-rays) and neutrons. Particle size, shape and size distributions can be obtained using light scattering techniques. Since the properties exhibited by colloidal systems are greatly affected by the particle size, size distribution and shape, they form important parameters for process and quality control.

Typically, in industrial applications one has to deal with concentrated suspensions containing as much as 40% solids. However, currently available light scattering techniques for extracting size and size distributions rely on theories based on dilute suspensions such as the Debye and Mie theories [1-4]. The fundamental assumptions made in the development of these theories are that single scattering is predominant and that the scattering centers are independent of one another. For colloidal dispersions at low electrolyte concentrations, strong inter-particle interactions lead to correlations in the particle positions even at relatively low concentrations. In such cases, the assumption of independent scattering centers breaks down. Also, in the light scattering regime, the single scattering approximation holds only for very dilute dispersions [1-3]. Therefore, to characterize the particle properties in dense suspensions by light scattering techniques using the single scattering approximation, the samples have to be diluted to a great extent, usually about 100 to 10,000 times. Online/atline process monitoring using conventional technology is thus extremely difficult. To circumvent the problem of multiple scattering, investigations of concentrated dispersions have been generally carried out using neutron scattering [5]. However, this approach is not yet feasible for online process monitoring.

More recently, for the case of systems of non-interacting particles the transport theory of light [6] has been used to deal with multiple-scattered systems. Within the framework of the transport theory, the effect of structure due to particle interactions can be included in an approximate fashion by assuming that such effects only modify the single particle scattering cross-section. In the past decade, this approach has been used to study correlated media with short-range interactions arising in systems of hard spheres [7-14]. Dick and Ivanov [11] have shown that in the case of a system of uncharged hard spheres, this approximation works well when the size parameter less than 3.5. As the size parameter increases, the deviations become significant at high concentrations. Further, the approximation holds only for systems in which the transport mean free path of the photons is much larger than the distance over which the correlations between particles exist. Thus the deviations become greater when the system becomes more ordered. Ordering over several particle diameters can be expected at lower concentrations when the interactions are long-ranged as would be in the case of charged particles in an electrolyte when the electrolyte concentration is not high enough to drastically screen the interactions.

A measurement-based (optical sampling) approach to circumvent the problem of multiple scattering have been implemented by a few groups. Fiber-optic measurement systems to study concentrated suspensions by optical sampling have been developed both using Dynamic Light Scattering (DLS) [15-18] and static light scattering techniques [19]. This approach basically consists of using a fiber probe with the distance between the source and detection fibers sufficiently small so that the transmitted light collected by the

detection fiber is essentially that which has undergone no more than a single scattering event. Thus, it will be possible to characterize suspensions of much higher concentrations by means of a fiber optic sensor using the theories that hold for dilute suspensions. The references mentioned here however neglect the presence of inter-particle interactions and therefore neglect the effect of the fluid structure on the scattered radiation.

Clearly, the interpretation of spectra of concentrated suspensions involves addressing two issues viz. multiple scattering effects and the effect of micro-structure due to inter-particle interactions. This paper focuses on the issue of micro-structure within the single scattering regime on the interpretation of spectra. It is assumed that the multiple scattering effects are circumvented using optical sampling. Specifically, the focus is on monodisperse dispersions of charged spherical particles suspended in low to moderate electrolyte concentrations and therefore particle interactions are medium to long-ranged.

In this paper, a semi-empirical representation of the microstructure of a dispersion of charged particles is proposed. The semi-empirical representation accounts for the effect of structure/ordering in a dispersion of interacting particles on light scattering by using the Percus-Yevick Hard-Sphere (PY-HS) model with “effective” hard-sphere parameters. The “effective” hard-sphere parameters are obtained such that the structure (as described by the structure factor) generated by the PY-HS model using these “effective” parameters match the structure factor of the dispersion under consideration. Basically, this approach assumes that the microstructure arising due to complex inter-particle interactions can be represented with sufficient accuracy by an adjustable two-parameter model which in this case is the PY-HS model.

The next section gives an outline of the scattering theory used to interpret spectra of dispersions of interacting particles and the effect of the microstructure of the dispersion on the spectra and its interpretation.

2. Interpretation of spectra of a dispersion of interacting particles

Consider a dispersion of interacting particles. Then under conditions where the single scattering approximation is valid, the transmitted intensity is given by

$$\frac{I_t(\lambda)}{I_0(\lambda)} = \exp[-\rho\sigma_t(\lambda)l] \quad (1)$$

where I_0 and I_t are the intensities of incident and transmitted light respectively, ρ is the number density of particles, $\sigma_t = \sigma_s + \sigma_a$ is the total cross-section of a single particle, σ_s is the scattering cross-section, σ_a is the absorption cross-section, λ is the wavelength of the incident radiation and l is the distance between the source and detection fibers. In this investigation, only situations where absorption is negligible will be considered and therefore $\sigma_t = \sigma_s$ which is given by,

$$\sigma_s(\lambda) = \int_0^{2\pi} \int_0^\pi F(\theta, \lambda, d) S(\theta, \lambda, V_T) \sin\theta d\theta d\phi \quad (2)$$

and Eq. (1) can be rewritten as,

$$\frac{-1}{l} \ln\left(\frac{I_t(\lambda)}{I_0(\lambda)}\right) = \rho \int_0^{2\pi} \int_0^\pi F(\theta, \lambda, d) S(\theta, \lambda, V_T) \sin\theta d\theta d\phi \quad (3)$$

where $F(\theta, \lambda, d)$, the differential scattering cross-section of a particle, is a measure of the fraction of incident power scattered by a particle in a given direction and $S(\theta, \lambda, V_T)$, the

static structure factor, is a measure of correlation of the particle positions and is dependent on the total pair potential V_T which in turn is a function of diameter in addition to other factors such as particle charge, salt concentration and particle concentration. In the absence of inter-particle interactions Eq. (3) reduces to,

$$\frac{-1}{l} \ln \left(\frac{I_t(\lambda)}{I_0(\lambda)} \right) = \rho \int_0^{2\pi} \int_0^\pi F(\theta, \lambda, d) \sin \theta d\theta d\phi \quad (4)$$

For spherical particles, $F(\theta, \lambda, d)$ can be obtained exactly using Mie theory by numerical solution of Maxwell's equations [3]. Closed form analytical expressions for $F(\theta, \lambda, d)$ can be used for particles that are very small or very large compared to wavelengths or if the optical properties of the medium in which the particles are suspended are similar to those of the particles [3]. The particle size can then be estimated by inverting the integral equation Eq.(4).

For systems where particle interactions are significant, in addition to an expression describing the differential cross-section, an expression for the structure factor is needed to carry out the inversion. Given the pair interaction energy, the radial distribution function $g(r)$ and hence the static structure factor can be obtained using the Ornstein-Zernicke equation along with some closure approximations [5, 20, 21]. However, these approximations usually do not give $g(r)$ or its Fourier counterpart, the static structure factor with sufficient accuracy [22]. Further, the more accurate approximations like the Percus-Yevick or the Hypernetted Chain approximations are numerically too intensive to use as part of the inversion problem.

A computationally simple and accurate representation of the structure factor is key for the successful inversion of Eq. (3). In the next section a hybrid approach which uses the hard sphere model with the hard sphere parameters treated as adjustable parameters is proposed to develop a semi-empirical representation of the static structure factor of a dispersion of charged particles.

3. A hybrid method to represent structure factor

A plausible approach that could provide a numerically simple and fast computation of the structure factor is to run a number of well-characterized samples with different particle sizes and magnitude of interactions (which can be varied by varying the particle size, volume fraction and salt concentrations) that will span the range of conditions that will be encountered by the system under consideration and experimentally obtain the structure factor. In these cases, since the particle sizes and volume fractions are known, the spectra obtained can be inverted (using Eq. (3)) to obtain the structure factor for the different conditions. The structure factor can then be fitted to simple closed form solutions obtained by using for example the PY-HS model. The estimated “effective” hard-sphere parameters can then be represented as a function of the system variables viz. particle diameter, volume fraction and the Debye parameter κ which is given by [23]

$$\kappa = \left(\frac{2n_0(ze)^2}{\epsilon\epsilon_0 k_B T} \right)^{1/2} \quad (5)$$

where n_0 is the concentration of micro-ions, z is the valence of the micro-ions, e is the electron charge, ϵ_0 is the dielectric permittivity of free space, ϵ is the relative dielectric constant of the medium, k_B is the Boltzmann constant and T is the temperature.

The semi-empirical representation accounts for the effect of structure/ordering in a dispersion of interacting particles on light scattering by using the Percus-Yevick Hard-Sphere model with “effective” hard-sphere parameters. The “effective” hard-sphere parameters are obtained such that the structure (as described by the structure factor) generated by the PY-HS model using these “effective” parameters match the structure factor of the dispersion under consideration. Basically, this approach assumes that the microstructure arising due to complex inter-particle interactions can be represented with sufficient accuracy by an adjustable two-parameter model which in this case is the PY-HS model.

If a sufficiently accurate representation can be found, then a system of integral equations represented by Eq. (3) at each wavelength can be solved using for example, the least squares method to obtain particle size, volume fraction and the Debye parameter for a sample. Successful implementation of this approach depends on two key factors: One is the availability of an analytical expression for describing the static structure factor that can be used to fit the experimental data accurately over a wide range of system parameters. The second is the ability to build empirical models that relate the parameters of the analytical expression to the system parameters with sufficient accuracy. These two considerations were examined using data generated from Monte Carlo simulations.

The reason for using simulations is two-fold. One is that to successfully use the optical sampling approach to completely characterize dispersions of interacting particles, the proposed semi-empirical method for extracting information from a spectrum should be feasible. Simulations will save time and money required for designing and building an instrument configuration (e.g. for optical sampling) if this method of extracting information does not work. So a feasibility study of the proposed semi-empirical method through simulations is advisable before proceeding further. Secondly (and more important), when evaluating the scope and efficacy of an empirical treatment such as the one proposed in this paper, experimental data with the errors in measurement (both in terms of particle properties such as size, shape, distribution, volume fraction and in terms of errors in the measured spectra) could lead to misleading results. Cancellation of errors could potentially lead to better agreement between calculated and experimental values. In equation 2, both the differential cross-section and the static structure factor are inside the integral. Thus any errors in the calculation of these quantities tend to be “smoothed out” when computing the scattering cross-section. As a result, the computed value for the scattering cross-section would still show good agreement with experimental data even if the structure factor (or the differential cross-section) values and “profile” (shape of $S(Q)$ or $F(Q)$ as function of Q) are very different from the actual values. Therefore, in the evaluation of any method for accounting for the structure factor, the use of simulations will be a good first step.

3. Data generation by Monte Carlo Simulations

Static structure factor data for charged polystyrene spheres suspended in water were generated using Monte Carlo simulations for a wide range of system variables i.e. particle sizes, volume fraction and salt concentrations [24]. The total interaction between two particles was modeled as the sum of hard sphere, van der Waals and electrostatic interactions. The van der Waals interactions between two spheres were modeled using the expression of Clayfield et al. [25]. This equation is an improvement over the more generally used Hamaker equation in that it takes into account retardation effects. While like the Hamaker equation, this expression does not take into account many-body effects, it shows much better agreement with values obtained from the more rigorous Lifshitz theory for van der Waals interactions [26]. The electrostatic interactions were modeled according to the Jellium approximation [27]. This model is an extension of the classical Poisson-Boltzmann equation in that it accounts for the excess counter-ions which become significant at low salt concentrations. These interaction models were chosen so that the simulations represent the qualitative behavior exhibited by a real system over the whole range of electrolyte concentrations.

The simulations were carried out using the Metropolis Monte Carlo method [28,29]. All the simulations in this study started with an initial configuration in which the particles were set up in a face centered cubic (fcc) lattice. The number of particles N was chosen such that the total pair potential was less than $10^{-5} k_B T$ at a distance equal to $L/2$ where L is the length of the simulation box. The spherical cut-off distance r_c was chosen according to this criterion, thus ensuring that r_c is always less than or equal to $L/2$. In most cases, $N = 500$ was more than sufficient to ensure that the criterion was satisfied,

except for high volume fractions, in which case N was set to 864 or 1372. In all the simulations that were run, the number of cycles (one cycle consists of N particle moves) for equilibration was set at 5000 in order to ensure that the system has sufficiently equilibrated. After equilibration, the simulation was run for 8000 cycles and the configurations were stored every 15 cycles. The static structure factor was computed from the stored configurations. A total of 41 samples spanning a range of particle sizes, volume fractions and salt concentrations were generated.

4. Results and discussions

The Percus-Yevick hard-sphere model (PY-HS) with its two parameters, the hard-sphere volume fraction ϕ_{hs} and the hard-sphere diameter d_{hs} was used to fit the structure factor of each sample using nonlinear regression. For the PY-HS model, the static structure factor is given by [23],

$$\frac{1}{S(Q)} = 1 + \frac{24}{x^3} \left\{ \begin{array}{l} a(\sin x - x \cos x) + b \left[\left(\frac{2}{x^2} - 1 \right) x \cos x + 2 \sin x - \frac{2}{x} \right] \\ + \frac{\phi_{hs} a}{2} \left[24/x^3 + 4(1 - 6/x^2) \sin x - (1 - 12/x^2 + 24/x^4) x \cos x \right] \end{array} \right\} \quad (6)$$

where $x = kd_{hs}$, $\phi_{hs} = \pi d_{hs}^3 \rho_{hs} / 6$, $a = (1 + 2\phi_{hs})^2 (1 - \phi_{hs})^{-4}$, $b = -3\phi_{hs}(\phi_{hs} + 2)^2 / 2(1 - \phi_{hs})^4$, ρ is the number density and Q , the magnitude of the scattering vector is given by,

$$Q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (7)$$

where λ is the wavelength of radiation in the medium, and θ is the scattering angle.

The results of fitting the hard-sphere model for the 41 samples are given in Table 1 where the “effective” PY-HS parameters that give the best least-squares fit to the

“experimental” structure factor for a dispersion with a particular set of system parameters are shown. A visual comparison of the actual versus fitted $S(Q)$ is shown in figure 1 for typical cases. From the table and the figure, it can be seen that an excellent fit is obtained using the two-parameter Percus-Yevick hard-sphere model. The next step is to find if these parameters could be represented as a function of particle diameter, volume fraction and the Debye parameter so that an empirical model is available for estimating the “effective” PY-HS parameters given the system variables.

Only linear models relating the “effective” PY-HS parameters to the system variables were considered. Stepwise regression [30] was used to choose the variables for the regression model and to estimate the parameters. All 41 samples covering a wide range of particle sizes ($d = 50\text{-}800\text{nm}$), volume fractions ($\phi = 0.001 - 0.2$), and salt concentrations ($M = 1.0\text{e-}3 - 1.0\text{e-}6\text{M}$) were used to build the models. The model obtained for d_{hs} is given by

$$d_{hs} = b_0 + b_1 d + \frac{b_2}{\kappa} + \frac{b_3}{\kappa^2} + \frac{b_4}{\phi^2} + \frac{b_5}{d} + \frac{b_6}{\phi \kappa} + b_7 \kappa d \quad [8]$$

where $b_0 = 0.0045 \pm 0.0007$, $b_5 = -3290 \pm 601$, $b_6 = -0.019 \pm 0.003$, and $b_7 = 2.5 \pm 0.27$. The confidence intervals for the coefficients are reported here as one standard error. The standard error of estimating d_{hs} was 17.1 nm. Figure 2 shows the estimated d_{hs} versus the actual values.

A model for ϕ_{hs} was developed in a similar fashion. This model is given by

$$\phi_{hs} = c_0 + c_1 \phi^{\frac{3}{2}} + \frac{c_2}{\kappa d} + c_3 \kappa^{\frac{3}{2}} + \frac{c_4}{(\kappa d)^{\frac{2}{3}}} + \frac{c_5 d}{\sqrt{\kappa}} + c_6 \log\left(\frac{\kappa d}{\phi}\right) + c_7 \sqrt{\log\left(\frac{d}{\kappa}\right)} \quad [9]$$

where $c_0 = -0.66 \pm 0.17$, $c_1 = 1.08 \pm 0.2$, $c_2 = -0.5 \pm 0.11$, $c_3 = 4.35 \pm 0.69$, $c_4 = 0.696 \pm 0.124$, $c_5 = -2.1e-5 \pm 3.71e-6$, $c_6 = 0.137 \pm 0.006$, and $c_7 = 0.585 \pm 0.055$. The standard error of estimating ϕ_{hs} was 0.021. A plot of the estimated versus the actual values is shown in figure 3.

However, in many practical situations, the system parameters, specifically the electrolyte concentration does not vary as widely as has been considered here. Thus simpler and more accurate models may be built by reducing the range spanned by the electrolyte concentration. The possibility of building simpler and more accurate models by reducing the range of system parameters was investigated. For this purpose, a subset of the 41 samples (a total of 23 samples) with particle radius 50-400nm and salt concentrations $10^{-3} - 10^{-4}$ M were analyzed. As before stepwise regression was used for building the models. The model for d_{hs} so obtained was,

$$d_{hs} = b_0 + b_1 d + \frac{b_2}{\kappa} + \frac{b_3}{\kappa^2} + \frac{b_4}{\sqrt{d}} + b_5 \kappa d \quad (10)$$

with $b_0 = 151 \pm 17$, $b_1 = 1.124 \pm 0.017$, $b_2 = -9 \pm 1.7$, $b_3 = 0.369 \pm 0.05$, $b_4 = -602 \pm 112$, and $b_5 = -1.4 \pm 0.15$. The standard error of estimation was 3.9nm compared to 17.1nm when the full range of parameters is used. As would be expected, the model structure is simpler than previously obtained. Similarly, for ϕ_{hs} , the model is given by,

$$\phi_{hs} = c_0 + \frac{c_1}{\phi^{\frac{3}{2}}} + \frac{c_2}{\sqrt{d}} + c_3 \kappa d + \frac{c_4 \kappa d}{\phi} + c_5 \log\left(\frac{\kappa d}{\phi}\right) \quad (11)$$

where $c_0 = 1.83 \pm 0.04$, $c_1 = 1.17e-4 \pm 1.19e-5$, $c_2 = -1.55 \pm 0.14$, $c_3 = 0.0027 \pm 0.0002$, $c_4 = 8.3e-5 \pm 9.4e-6$, and $c_5 = -0.25 \pm 0.007$. The standard error of estimation was 0.0068

compared to 0.021 when the full range is used and again the model structure is simpler than previously obtained.

The foregoing analysis suggests that the simple PY-HS model may be adequate for fitting the experimental structure factor data to desired accuracy over a range of experimental conditions that would be found in practice. Clearly, the “effective” PY-HS parameters so obtained contain information about the system variables that define the particle interactions and therefore the fluid structure. Thus the approach will also allow the extraction of extra information such as the Debye parameter and the static structure factor.

While the “effective” PY-HS parameters contain information about the system variables and the structure of the system, the accuracy with which the structure of the system is reproduced using the semi-empirical method will dictate the accuracy of the estimated particle size, concentration and Debye parameter. Notice that Eq. (3) with Eq. (6) used for the structure factor leads to the possibility of strong correlations between the estimated system variables. This correlation could have an effect both on the inversion of Eq. (3) and on how the errors in the “effective” PY-HS parameters and the error in the experimentally obtained spectra will affect the estimation of the system variables.

The semi-empirical method delineated in this manuscript was investigated in the context of the single scattering regime to account for particle interactions. However, it could potentially be used when multiple scattering is taken into account through the

transport theory (provided the transport mean free path of the photons is much larger than the distance over which the correlations between particles) since the problem would then be the same as extracting information from Equation (3) with the RHS equal to the bulk scattering coefficient μ_s .

5. Conclusions

In this paper, a semi-empirical representation of the static structure factor of charged colloidal dispersions is proposed to account for the effect of particle interactions in the single-scattering regime. It was shown using data generated by Monte Carlo simulations, that the static structure factor of a dispersion with complex inter-particle interactions can be accurately described by the two parameter Percus-Yevick hard-sphere model by using “effective” PY-HS parameters. Further, these parameters can be related to the system parameters (particle size, particle concentration and electrolyte concentration) through an empirical model by fitting experimental data. Analysis of data generated by Monte Carlo simulations suggests model structures that give good estimates of the “effective” PY-HS parameters over a broad range of experimental conditions. This study indicates that using multi-wavelength (and/or multi-angle) spectra, information regarding the fluid structure, particle size, particle concentration and the Debye parameter could be extracted when a semi-empirical method is used for describing the fluid structure.

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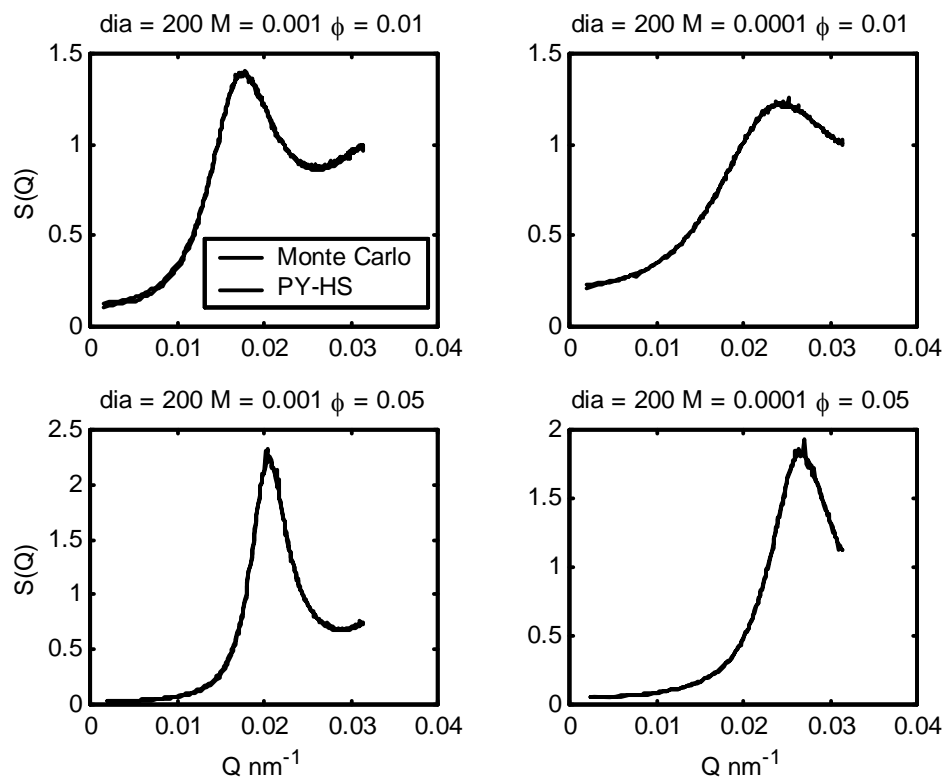


Figure 1. Plots comparing structure factors obtained from fitting the PY-HS model to the actual values from MC simulations.

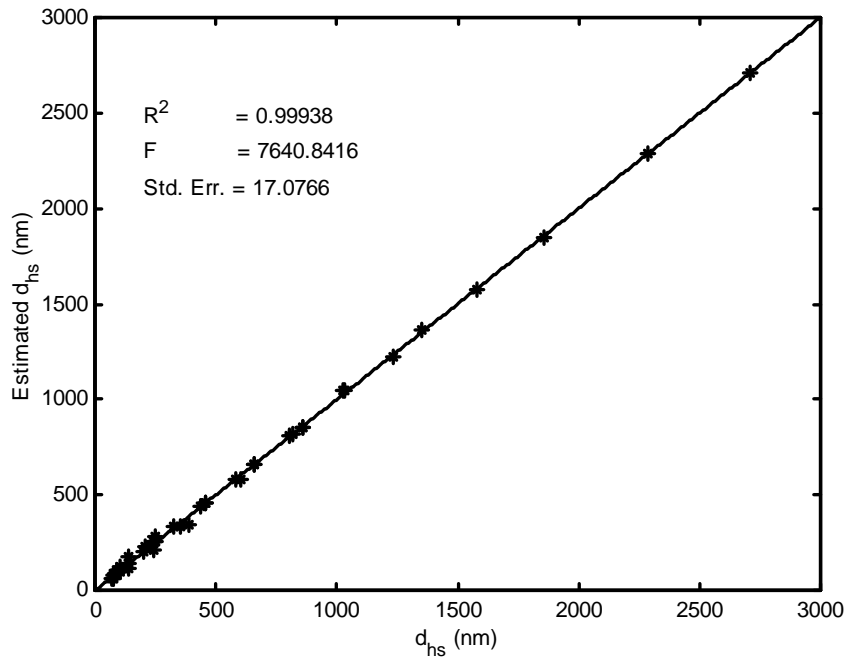


Figure 2. Plot of values of d_{hs} versus values estimated using the model given by (8).

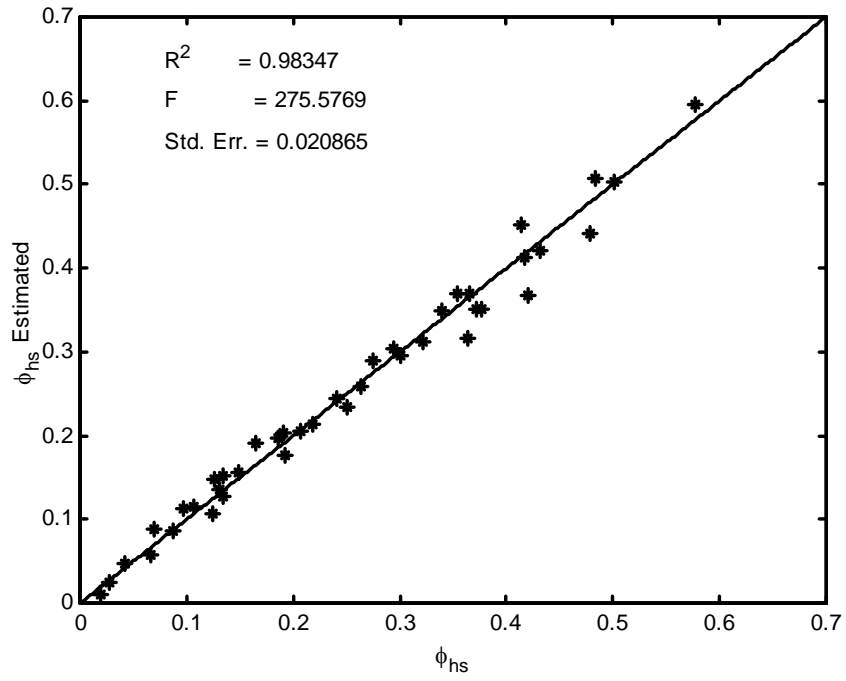


Figure 3. Plot of values of ϕ_{hs} versus values estimated using the model given by (9).

Table 1. Results from fitting the Percus-Yevick hard-sphere model to $S(Q)$ obtained from MC simulations.

Radius (nm)	Volume Fraction	Salt Conc. mol/l	ϕ_{hs}	d_{hs} (nm)	R^2	RMS Error
25	0.01	1.0E-03	0.042394	82.2901	0.9966	0.00518
25	0.01	1.0E-04	0.19235	141.0181	0.98667	0.03582
25	0.01	1.0E-06	0.34023	205.1999	0.97839	0.05632
25	0.05	1.0E-03	0.18663	79.3103	0.99869	0.00867
25	0.05	1.0E-04	0.37595	100.7292	0.99873	0.02537
25	0.05	1.0E-06	0.41342	104.0642	0.99867	0.03167
25	0.1	1.0E-03	0.32137	75.9953	0.99834	0.00568
25	0.1	1.0E-04	0.47791	88.0753	0.99544	0.00646
25	0.1	1.0E-06	0.50196	90.3645	0.99563	0.00587
25	0.2	1.0E-03	0.48307	69.6371	0.997	0.00120
25	0.2	1.0E-04	0.57757	74.3731	0.99787	0.00044
50	0.01	1.0E-03	0.027873	141.7355	0.99778	0.00283
50	0.01	1.0E-04	0.13056	242.7008	0.9903	0.01512
50	0.01	1.0E-06	0.43157	434.0006	0.98114	0.05639
50	0.05	1.0E-03	0.1337	140.2665	0.99913	0.00655
50	0.05	1.0E-04	0.36337	198.596	0.99381	0.03253
100	0.01	1.0E-03	0.019524	250.4268	0.99774	0.00208
100	0.01	1.0E-04	0.068758	385.1295	0.9992	0.00456
100	0.05	1.0E-03	0.096918	249.9689	0.99974	0.00259
100	0.05	1.0E-04	0.26372	354.0115	0.99769	0.01428
100	0.1	1.0E-03	0.19004	248.6717	0.99979	0.00345
100	0.1	1.0E-04	0.42074	326.5261	0.99712	0.02539
100	0.2	1.0E-03	0.36514	245.1698	0.99958	0.00809
200	0.01	1.0E-06	0.3541	1347.7219	0.99301	0.03222
200	0.05	1.0E-04	0.16531	600.0881	0.99944	0.00512
200	0.1	1.0E-03	0.14884	456.9504	0.9998	0.00283
200	0.1	1.0E-04	0.29993	580.8468	0.99932	0.00849
200	0.2	1.0E-03	0.29478	455.3721	0.99983	0.00416
300	0.001	1.0E-06	0.086523	2708.6792	0.99651	0.00944
300	0.01	1.0E-06	0.27531	1857.5472	0.99507	0.02171
300	0.05	1.0E-03	0.066475	660.261	0.99957	0.0026
300	0.05	1.0E-04	0.12671	820.6837	0.99977	0.0029
300	0.05	1.0E-06	0.41687	1232.7091	0.99671	0.02693
300	0.1	1.0E-03	0.13341	660.3314	0.99977	0.00289
300	0.1	1.0E-04	0.24065	806.8082	0.99965	0.0051
400	0.01	1.0E-06	0.2182	2287.6149	0.9943	0.0166
400	0.05	1.0E-04	0.10708	1033.4509	0.99934	0.00351
400	0.05	1.0E-06	0.37258	1582.2821	0.99788	0.01887
400	0.1	1.0E-03	0.12512	860.8015	0.99931	0.00392
400	0.1	1.0E-04	0.20766	1022.8465	0.99977	0.00375
400	0.2	1.0E-03	0.24994	860.2854	0.999983	0.00370